Plastic strain-induced grain refinement in the nanometer scale in a Mg alloy

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Received 31 August 2006; received in revised form 18 September 2006; accepted 18 September 2006
Available online 28 November 2006

Abstract

By means of surface mechanical attrition treatment, nanometer-sized grains (with an average size of 30 ± 5 nm) were generated in the surface layer of a single-phase AZ91D alloy. Transmission electron microscopy investigations showed that the strain-induced grain refinement process in AZ91D alloy includes three steps. At the initial stage twinning dominates the plastic deformation and divides the coarse grains into finer twin platelets. With increasing strain, double twins and stacking faults form and a number of dislocation slip systems are activated, including basal plane systems, prismatic plane systems and pyramidal plane systems. As a result of the dislocation slip along these systems and of the cross slips, high-density dislocation arrays are formed which further subdivide the twin platelets into subgrains. Obvious evidence of dynamic recrystallization were identified within the high-strain-energy subgrains with a further increase of strain, leading to the formation of nano-sized grains in the surface layer.

Keywords: Magnesium alloy; Grain refinement; Twinning; Dynamic recrystallization; SMAT

1. Introduction

Magnesium alloys have attracted great attention with regard to their application in transportation as the industry seeks to reduce weight and increase fuel efficiency [1]. However, the low strength, poor wear resistance and low corrosion resistance of these alloys limit their use in industrial practice. Non-traditional surface treatment is one of the main areas being researched to solve the problem. Surface mechanical attrition treatment (SMAT) has been proven to be an effective approach to obtain a hard layer owing to the formation of nanocrystalline structure in the treated surface [2,3]. The basic principle of SMAT is the generation of plastic deformation in the surface layer of a bulk material by means of the repeated multidirectional impact of flying balls (GCr15 steel in most cases) on the sample surface. The plastic deformation in the surface layer under the high strain rate results in a progressive refinement of coarse grains into a nanometer regime. The technique has been successfully applied to a number of alloy systems. However, previous experimental results [2–9] show that the mechanism of grain refinement varies with materials. In most of the published works, there are actually two factors governing the grain refining process: the stacking fault energy (SFE) and the number of slip systems in the metals. Lu et al. [3] pointed out that for base-centered cubic (bcc) Fe with a high SFE (about 200 mJ/m²), formation of dislocation walls and dislocation tangles are responsible for the refinement because twinning is difficult; for face-centered cubic (fcc) Cu that has a medium SFE (about 78 mJ/m²), the formation of dislocation cells and twins results in grain refining [9]; while for fcc austenite with a low SFE (17 mJ/m²), the combination of formation of dislocation arrays and twins, together with stress-induced martensitic transformation, are the major reason for the formation of nanocrystallites. Recently, Wu and co-workers [6]...
reported a grain refinement mechanism for hexagonal close packed (hcp) pure Co that has a low SFE (27 ± 4 mJ/m²). Zhu et al. [7] presented an investigation on the nanostructure formation mechanism of SMATed Ti with a rather high SFE (>300 mJ/m²). Despite the large difference between SFEs of these two hcp metals, twinning appears to be the dominant deformation mechanism at low strain, which illustrates that twinning might be a common deformation manner in materials with an hcp structure.

As a simple hcp structured metal, Mg and its alloys have SFEs within the range of 60–78 mJ/m², which is higher than that of Co and lower than that of Ti. Besides, Mg has a much lower melting temperature (660 °C) than Co and Ti, which corresponds with its lower recrystallization temperature. In the past decade, severe plastic deformation (SPD) approaches [10], such as equal channel angular extrusion (ECAB) [11–13], accumulative roll bonding (ARB) [14] and high-pressure torsion (HPT), have been applied to the grain refinement of Mg alloys on bulk materials. Twinning and dynamic recrystallization (DRX) were found to be responsible for grain refinement for most processes. But in most of these cases, the grain size of the final refinement structure is in the micrometer or submicrometer range. It is not clear what dominates the grain refinement mechanism if grain size can be further divided into the nanometer scale. So it is of interest from both the scientific and the practical points of view to investigate the strain-induced grain refinement mechanism in the Mg system by using SMAT, which, in most metal systems, has been proven to be able to produce a nanocrystalline structure in the surface layer of the treated material.

2. Experimental methods

The material used is commercial AZ91D alloy with a chemical composition of 8.47Al–0.69Zn–0.14Mn (wt.%). Plate samples 100 × 100 × 12 mm³ in size were cut from the as-received ingot and solution treated at 413 °C for 24 h followed by water quenching. Samples were then ground with silicon carbide sand paper to grade 1000 on both sides. Previous work [2–9] indicates that this surface finish is good enough for SMAT.

The SMAT was carried out using an SNC-II surface nanocrystallization testing machine. In order to optimize the SMAT time for the solid solution-treated AZ91D alloy, the treatment was carried out over a range of periods from 5 to 60 min. After SMAT, the grain size in the top surface layer of the treated samples was determined by X-ray diffraction (XRD), which was carried out in a Rigaku DMAX/2400 diffractometer with operation voltage at 40 kV using Cu Kz radiation. The grain size was calculated using the Scherrer–Wilson equation [15]. Variation of hardness along the depth from the treated surface was determined by a MVK-H300 Vickers hardness testing machine, with a load of 5 g and a loading time of 10 s. In order to investigate the grain refinement process and mechanism during SMAT, it is necessary to examine the microstructure change at different plastic deformation steps. As the deformation always starts from the top surface layer and then extends to the substrate along the depth from the surface, sections in the specimen at different depths from the surface correspond to different deformations and strains. Hence, the examination of the microstructure in these different regions can reveal the microstructure evolution at different plastic strains, and the grain refinement process and mechanism can consequently be understood. Transmission electron microscopy (TEM) specimens were cut off from three different regions in the SMATed samples, which correspond to three different depth ranges: less than 100, 100–600 and 600–1500 μm from the top surface. These three regions represent the three deformation steps which will be detailed in the ensuing section. The TEM specimen preparation process is as follows: 0.3-mm-thick slices were cut off from different regions followed by mechanical grinding to 0.03–0.05 mm. For the slices cut from the top surface layer (less than 100 μm), only the side opposite to the surface of the treated block sample was ground; the other slices were ground on both sides. Then the thin foils were ion milled at room temperature in a Gatan PIPS with a small incident angle till perforation. All the thin foils were examined in a JEOL 2010 TEM operated at 200 kV.

3. Results and discussion

X-ray diffraction result shows that a single hcp phase was obtained after solid solution treatment at 413 °C for 24 h followed by water quenching. No Mg₁₁₇Al₁₂ (β) phase was detected in the samples. It is found that the grain size of the surface layer is reduced with the increase of SMAT time and the smallest grains were obtained with the sample having been SMATed for 20 min. When the SMAT time is longer than 20 min, the grain size starts coarsening. The reduction of the grain size with increasing treatment time is due to the accumulation of plastic deformation and strain in the surface layer. However, the grain coarsening after 20 min is a new phenomenon compared with the result from Fe [4]. It is related to DRX. Unlike the alloy systems previously reported [3–9], DRX is considered to be a major process in plastic strain-induced grain refinement in the nanometer scale in Mg alloys, and will be discussed in detail in the following sections. All the subsequent results were got from the sample that had been SMATed for 20 min.

3.1. Improvement of micro-hardness after SMAT

Fig. 1 shows the variation of micro-hardness with distance from the SMATed surface to the substrate, together with the corresponding grain size of the region. From this figure the thickness of the total deformation layer generated by SMAT in AZ91D alloy can be identified to be about 1500 μm. This is a much greater thickness than that of other alloys, which are normally only a few hundred micrometers thick [6,7]. In addition, it can also be seen that
the hardness at the top surface layer is about twice that of the substrate. The corresponding value of grain size increases with increasing distance from the top surface. In the following section, the microstructure evolution in the sections that are 1500 μm below the surface will be discussed in detail.

### 3.2. TEM investigations of the grain refinement process

As stated above, the sections at different depths of the SMAT samples correspond to different plastic deformation mechanisms. Previous studies [3–7] indicated that the SMAT-affected zone in a sample could be divided into three regions: the nanocrystalline region (NC), which is close to the top surface, followed by the submicrocrystalline region (SMC) and the deformed region, which is close to the matrix. Therefore, the microstructure characterization at each region will provide information about the strain-induced grain refinement process during SMAT treatment.

#### 3.2.1. The deformed region

According to the result shown in Fig. 1, the section at 600–1500 μm below the treated surface is equivalent to the deformed region, where severe plastic deformation occurred. TEM examination verifies that the deformation is predominated by deformation twinning (DT) in the present alloy. Thus this region is also termed the DT region. Fig. 2 presents typical TEM micrographs showing the deformation twins. The selected area diffraction pattern in Fig. 2c shows that the twin system is \{1012\}/\{1011\}. The twinning interface is determined to be \(\{1012\}\). In
magnesium alloys, dislocation slip, twinning and fracture are the three major mechanisms involved in the release of stress. These three mechanisms compete with each other within a large temperature range. Due to the limited slip system at room temperature in hcp Mg alloys, twinning has been theoretically and experimentally proven to be the dominant model that is responsible for plastic deformation. Although several twinning systems have been experimentally observed causing plastic deformation in Mg alloys [16,17], the \( \{10\bar{1}2\} \) and \( \{10\bar{1}1\} \) twins are the two major twinning systems, the \( \{10\bar{1}2\} \) twin in particular. Due to the smallest twinning shear \( (s = 0.1302) \), \( \{10\bar{1}2\} \) twinning governs the deformation in ECAE, SPD and other compression processes [11,18]. In the present work, as only the \( \{10\bar{1}2\} \) twins are found in our TEM observations while the \( \{10\bar{1}1\} \) twins have never been observed, it is sobering to conclude that at the initial stage of the SMAT process of AZ91D alloy, the dominant mechanism of plastic deformation is \( \{10\bar{1}2\}/\{10\bar{1}1\} \) twinning.

In order to understand the substructure within the twins, an area including three adjacent twinning plates (marked by the square in Fig. 2a) was examined at higher magnification and the micrograph is shown in Fig. 2b, in which the twin boundaries (TB) and the (0001) basal plane are marked. Stacking faults (SFs) along the (0001) basal plane can be clearly observed in the middle plate in Fig. 2b. A high-resolution transmission electron microscope (HRTEM) lattice image with the \( \{10\bar{1}2\}\) twin boundary and the \( \{21\bar{1}0\}\) axis parallel to the electron beam is shown in Fig. 3, and further proves the existence of SFs in the twin. Previous work [6,7] has shown that the presence of SFs is a mutual characteristic in hcp metals after SMAT and it is related to the SFE. Metals with lower SFE normally involve a higher density of SFs. It is believed that formation of SFs is the key step to further dividing the twins into smaller grains in Mg alloys.

Another feature of the microstructure within this region is the dislocations and dislocation arrays that can be observed in the top and the bottom of twin plates in Fig. 2b. These dislocations lie either on the basal plane or on the non-basal planes, which can be either the prismatic planes or the pyramidal planes; this indicates that dislocation slip also contributes to the plastic deformation besides twinning. Meanwhile, double twins (second-level twins) formed within the existing twin plates are also frequently observed, as shown in Fig. 4. These double twins also make significant contributions to the subdivision of twins.

3.2.2. The submicrometer region

Above the deformed region (600–100 \( \mu \)m) comes the submicrometer region, as a result of the increased stress and higher strain compared with the deformed region. Fig. 5 shows a dislocation array lying on a plane that is close to and approximately parallel to the twin interface. Since the angle between the SF and the trace of the twin interface is close to 43°, the twin interface must be \( \{10\bar{1}2\}\). Hence, the dislocation array in Fig. 5 is a result of dislocation moving and piling up on the \( \{10\bar{1}2\}\) plane. In addition, it should be indicated that although, for the
reason of brevity, the dislocation walls or arrays on the basal plane are not shown, dislocation movement along \( \{0001\}/\{1120\} \) slip system governs the strain accommodation. In Mg alloy, dislocation slip on the \( \{0001\}/\{1120\} \) and \( \{1010\}/\{1120\} \) systems can only lead to strain along the \( a \)-axis; it is necessary to activate the pyramidal slip in order to adjust the \( c \)-axis strain. In fact, it has been proven that, apart from twinning deformation, the pyramidal slip system in hcp crystals can provide five independent deformation modes [19,20], and the slip direction \( \langle 112\rangle \) provides multidimensional plastic deformation. In addition, previous work [21,22] has also pointed out that the deformation conditions, such as temperature, strain rate and grain size, can significantly affect the operation of non-basal slip systems, especially the pyramidal. In the present work, SMAT can generate a considerable extent of deformations at an extremely high strain rate, which may also lead to a temperature increment. Therefore, it is feasible that non-basal plane slip in Mg alloys contributes to the plastic deformation.

Fig. 6 is a TEM micrograph showing the subgrains separated by dislocation arrays in a twin plate. It can be seen that these dislocation arrays (as indicated by the white arrows) lie on various planes that have different orientations. This further confirms that when the strain is high enough, dislocations not only move on basal planes, but also slip on prismatic and pyramidal planes in Mg alloy. The dislocation arrays that subdivide the twin platelets into subgrains as shown in Fig. 6 are not straight. The curvature of this dislocation arrays is a result of cross slips [23]. As the misorientation among subgrains A, C and E is minor, as shown in Fig. 6, so the dislocation arrays, unlike in fcc and bcc alloys, cannot significantly change the orientations of the subgrains in Mg alloys. Therefore, these dislocation arrays cannot be regarded as grain boundaries. It is also observed that a considerable number of dislocations exist in the grains, which may accommodate a high density of strain energy.

It is interesting to note that the dislocation arrays in Mg alloy are quite different from the dislocation walls in other fcc and bcc alloys [4,5,9,24,25]. Normally, the dislocation walls contain a high density of dislocations that may cause changes to the crystal orientations and eventually become grain boundaries. However, the dislocation arrays in Mg alloy do not contain a sufficient number of dislocations to induce the formation of grains with significantly different orientations. They can only subdivide the twin platelets into smaller parts that have less different orientations and store considerable strain energy. When the strain energy is high enough, it may lead to DRX, which will be discussed further in the following section. In addition, there are no dislocation tangles observed in AZ91D alloy, even though they play an important role in grain refinement in fcc and bcc alloys. The low density of dislocations and the lack of dislocation tangles in Mg are attributed to the less available slip systems compared with fcc and bcc metals.

Another very important feature of Mg is its low melting point, which is different from other hcp metals, such as Co and Ti. For AZ91 alloys, the melting point is even lower than that of pure Mg. A low melting point corresponds to a low recrystallization temperature. During the SMAT processing of AZ91D alloy, with increasing treatment time a higher strain is generated in the regions that are close to the top surface, which may lead to a further decrease in the recrystallization temperature. Simultaneously, the temperature of the samples is also raised due to the conversion of mechanical work to heat. Therefore, DRX may occur at certain strain level. Fig. 7a is a typical example of freshly formed clean new grains (marked as A and B) in the heavily deformed twin platelet (marked as C) near the twin interface. Within the white square frame in Fig. 7a, a newly

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Fig. 6. TEM bright field image (a) and dark field image (b) of the ultrafine regions within a twin platelet separated by dislocation arrays that slipped on basal, prismatic and pyramidal planes.
formed small grain can be clearly seen. The selected area diffraction pattern in Fig. 7b taken from this area is no longer sharp. Spots are elongated and discrete circles are formed, which indicates that the originally large grains or twin platelets start being divided into smaller grains with different orientations through DRX.

3.2.3. The nanocrystalline region

This region corresponds to the one that is less than 100 µm below the topmost surface. Fig. 8 is a typical example of the microstructure within this region. The continuous diffraction rings in the selected area diffraction pattern in Fig. 8b indicate that randomly oriented grains were obtained. The average grain size determined from the TEM micrographs is 30 ± 5 nm, which is very close to that from XRD, which is 26 nm. Fig. 9a shows a “clean” nanometer grain formed within a highly deformed subgrain along the boundary or dislocation arrays. This “clean” nanometer grain implies the elimination of strain even though there is still high strain in the surrounding area. The only possible way to generate such clean nanometer grains within a highly deformed area is DRX. Fig. 9b is another TEM micrograph taken from this region. The “clean” and strain-free equiaxed grains can only be the result of recrystallization. As mentioned above, Mg alloy has a low melting point and therefore a low recrystallization temperature. Additionally, the heavy plastic deformation at extremely high strain rates during the SMAT process leads to the conversion of mechanical work to heat. Although the heat may partially flow into the substrate and the surroundings, the temperature rise is substantial. The combination of these two effects leads to the occurrence of DRX.

Dynamic recrystallization has been previously observed in Mg alloys as an important grain refinement mechanism when grain size is refined to the micrometer range. Mohri

Fig. 7. TEM bright field image (a) and selected area diffraction pattern (b) showing the newly formed “clean” grains with different orientations through DRX.

Fig. 8. TEM micrograph showing nano-sized grains in the region 100 µm below the treated surface.

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Dynamic recrystallization has been previously observed in Mg alloys as an important grain refinement mechanism when grain size is refined to the micrometer range. Mohri
et al. [26] reported the superplasticity of a rolled AZ91 alloy due to the ultrafine microstructure resulting from DRX. Tan and co-workers [27] found that the grain refinement in AZ31 alloy during tensile test at various temperatures resulted from DRX. In addition, DRX has also been proven to be an efficient mechanism of grain refinement for Mg alloys in hot torsion [28], ECAP [29], rolling [26], compression [30], high temperature creep [31] and other deformation processes. However, these previously reported approaches of grain refinement by severe plastic deformation all seemed to fail to obtain refined grains in the nanometer scale. The difference between SMAT and the previously reported severe plastic processes, e.g. ECAP and HPT, may lie in the strain rate. In SMAT, the strain rate is estimated to be about $10^2$–$10^3$ s$^{-1}$, while the strain rates of ECAP and HPT are much lower. As presented in a paper about refining copper by using SMAT [9], strain rate plays a key role in refining grains into the nanometer region. The strain rates of ECAP and HPT are too low to induce enough twinning activity and to form nanometer grains.

Dynamic recrystallization is generally acknowledged to happen within temperature ranges from 0.5–0.6 to 0.9–0.98$T_m$ [32,33]. For pure Mg, 0.5$T_m$ corresponds to 193 $^\circ$C; the DRX temperature for AZ91D, therefore, could be even lower than this temperature. Moreover, Kaibyshev et al. [34] even claimed that DRX occurred at room temperature, which corresponds to 0.3$T_m$ in pure Mg when the strain is quite high. During the SMAT process, the repeated multidirectional impact of flying steel balls generates severe

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Fig. 9. (a) Strain-free nanometer grain formed in a highly deformed subgrain along the boundary through DRX; (b) equiaxed nano-sized grains formed by DRX within the region 100 $\mu$m below the treated surface and the inset is the corresponding histogram of grain size distribution.

Fig. 10. Schematic illustration of the grain refinement process of AZ91D alloy during SMAT.
plastic deformation and strain at very high strain rates in regions near the top surface. The high strain in the sample will decrease the DRX temperature. Combined with the heat effect, which will raise the temperature of the layer as discussed above, DRX occurs. It should be mentioned that DRX can significantly refine the grains, but with the increase of SMAT time the newly formed grains will be subject to growth. As a result, longer SMAT processing times may cause grain coarsening.

3.2.4. Mechanism of surface nanocrystallization of AZ91D alloy during the SMAT process

Based on the above discussions, the process and mechanism of surface nanocrystallization of AZ91D alloy during the SMAT process can be clarified. Fig. 10 is a schematic diagram showing this process. At the beginning, the plastic deformation is governed by twinning, which divides the original coarse grains into finer twin platelets. With increasing strain in the sample, double twins and stacking faults appear within the twin platelets. As the SMAT process continues, the higher strain activates the dislocation slip systems in the order: basal plane system, prismatic plane system and pyramidal plane system. As a result of dislocation movement along these planes and cross slips, high-density dislocation arrays are formed within the twin platelets. These dislocation arrays subdivide the twins into subgrains with storage of high strain energy. The high strain energy stored in the sample significantly decreases the recrystallization temperature. Simultaneously, the heavy plastic deformation at high strain rate would also raise the temperature of the sample. Once the temperature is higher than the recrystallization temperature, DRX takes place. As a result of DRX, nano-sized grains form in the regions near the topmost surface, where the highest strain is generated.

4. Conclusions

(1) Nanometer-sized grains (with an average size of 30 ± 5 nm) can be generated in the top surface layer of a single-phase AZ91D alloy through SMAT. The thickness of the nanostructured layer is about 100 µm.

(2) The nanocrystallization process during SMAT can be divided into three steps: twinning, which divides the coarse grains into twin platelet; formation of subgrains and dislocation arrays as subgrain boundaries through dislocation movements on both basal plane and non-basal plane slip systems; and DRX, leading to the formation of nano-sized grains.

Acknowledgements

The authors acknowledge financial support from the National Natural Science Foundation of China, Ministry of Science & Technology of China (No. 2005CB623604) and Australia Research Council (ARC) Discovery Project (DP0557213).

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